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# Synthesis and characterization of composite phase change material (CPCM) with SiO<sub>2</sub> and diatomite as endothermal-hygroscopic material

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## Abstract

This paper prepared a kind of CPCM/diatomite composite as hygroscopic phase change material. The SiO<sub>2</sub> of the CPCM was prepared with tetraethyl orthosilicate with sol–gel method, and a kind of alkane mixture was used as phase change material (PCM). The diatomite was used as hygroscopic material. We used scanning electronic microscope (SEM) to determine the microstructure of the composites. The heat absorbing/solidifying properties and thermal stability of the composites were measured with the differential scanning calorimeter (DSC) and thermo-gravimetric analyzer (TGA). The hygroscopic properties were also investigated. The measurement results indicated that the composites had good thermal control and hygroscopic properties.

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**Keywords:** Phase change material; silicon dioxide; thermal energy storage material; hygroscopic material

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## 1. Introduction

With the development of economy, energy demand is increasing quickly. Conventional fossil energy sources are limited, and the use of them lead to climate changes and environment pollution. Buildings account for about 40 percent of the world's total energy consumption, and more than 30% of the primary energy consumed in buildings is

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for the heating and air-conditioning system. In order to ensure adequate supplies of energy and to curtail the growth of CO<sub>2</sub> emissions, it is essential that building energy consumption is significantly reduced. One way this can be achieved is through the introduction of passive building design enabled by innovative sustainable building materials, for example the hygroscopic phase change material.

The indoor temperature, relative humidity and air quality are important environmental parameters of human comfort. To control the indoor environment at a comfort level, the internal sensible and latent heat loads must be removed by either active technologies or passive strategies. The research of coupled heat and moisture transfer in buildings and using passive strategies to create comfort indoor environment are timely and important research topics.

The ambient temperature during a day is fluctuant. In summer, the temperature in daytime may be high during the daytime, so it's not comfortable. But at night the temperature drops below the comfort temperature range. Phase change material (PCM) can absorb thermal energy when the temperature is high, and release thermal energy when temperature is low. The temperature of the phase change material is a constant during the phase change process. So using the phase change material to realize the regulation of temperature is an ideal way of energy saving. But some disadvantages of the PCM limit the use of it, for example the low conductivity, super-cooling degree and the difference between the phase change temperature during heating and cooling. So many encapsulation methods have been developed to overcome the drawbacks. In previous works, the materials used to encapsulate the phase change material are mainly organic materials, which are flammable and likely to release toxic. Therefore some inorganic materials have been used to encapsulate the phase change material. Chen et al. [1] prepared some microcapsules with SiO<sub>2</sub> as shell material. He et al. [2] developed a new silica encapsulation technique using sodium silicate precursor. Cao et al. [3] and Chai et al. [4] prepared some microcapsules with TiO<sub>2</sub> as shell material.

Relative humidity is related to human comfort and health closely. People may suffer from rheumatic and rheumatoid arthritis if working in high humidity areas for long time. When humidity is too low, dry air makes people skin chapped, and dry cough and hoarseness may occur. In order to maintain a relatively stable relative humidity, air conditioning system is used to dehumidify or humidify the indoor environment. Humidity is also fluctuant during a day like temperature, so hygroscopic material can be used to regulate the indoor relative humidity, which can keep the indoor environment healthy, but also reduce energy demand.

A hygroscopic phase change material was prepared in this paper. SiO<sub>2</sub> prepared with tetraethyl orthosilicate by sol-gel method was used as shell material. A kind of alkane mixture was used as phase change material. Diatomite has a good moisture sorption property, and it is a kind of healthy organic material. So the diatomite was used as hygroscopic material. The composites were prepared to be a composite thermal regulating and humidity controlling materials.

## 2. Experiment

### 2.1. Materials

Tetraethyl orthosilicate (TEOS) (Reagent grade, Tokyo Chemical Industry Company); Anhydrous ethanol (Reagent grade, Sinopharm Chemical Reagent Company); Distilled water; Hydrochloric acid (Reagent grade, Sinopharm Chemical Reagent Company); PCM (Industrial grade, Ruhr Technology Company); Diatomite (Industrial grade, Shanghai Liangjiang Titanium White Product Company)

### 2.2. Preparation of PCM/SiO<sub>2</sub> composite

100 g TEOS, 100 g anhydrous ethanol, 40 g PCM and 200 g distilled water were mixed in a beaker. The pH value of the solution was adjusted to 2–3 by using hydrochloric acid, and then the solution was stirred at a rate of 500 rpm with a magnetic stirrer at 40 °C. The three-dimensional network of SiO<sub>2</sub> was formed with the hydrolysis reaction and polymerization process of the TEOS. Then the PCM was encapsulated into the SiO<sub>2</sub> network. And the PCM/SiO<sub>2</sub> composite was named as CPCPM.

### 2.3. Preparation of endothermal-hygroscopic material

The CPCPM was rubbed to powder, and then dried in a low temperature dried oven for 24 h at 0 °C. The diatomite was dried in a vacuum oven for 10 h at 110 °C. Then the CPCPM and diatomite were mixed with mass ratio 1:4. The CPCPM/diatomite composite was obtained and denoted as CHPCM.

### 3. Characteristics of the CPCPM/diatomite composite

The microstructure of the CPCPM/diatomite composites was observed by a scanning electronic microscope (SEM, S-3400N, Hitachi Inc., Japan). The thermal properties and stability of the CPCPM/diatomite composites were measured by a differential scanning calorimeter (Pyris 1 DSC/TGA, Perkin-Elmer).

#### 3.1. Morphology of the CPCPM/diatomite composites

Fig.1 shows the SEM photos of the diatomite, CPCPM and CHPCM. It can be seen from Fig.1a that the diatomite has a porous structure, which can absorb moisture. The Fig.1b shows that the PCM was encapsulated in the  $\text{SiO}_2$  shell, which can prevent the melted PCM from leaking. And the Fig.1c shows that the CPCPM is dispersed in diatomite, and there is no conglomeration of the CPCPM.

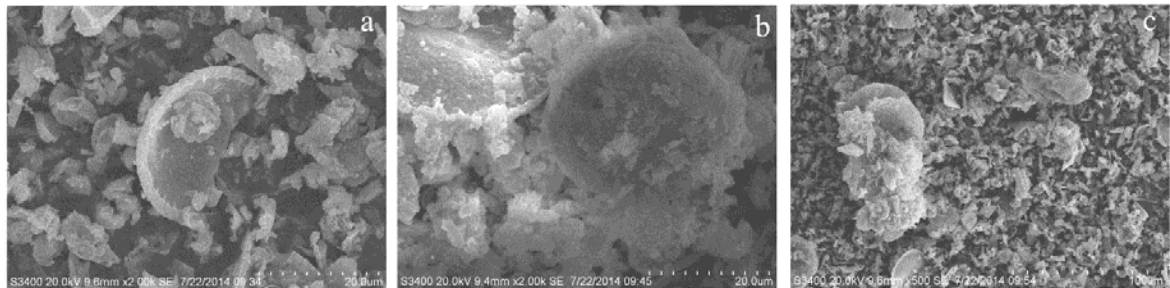


Fig. 1. The SEM of (a) diatomite; (b) CPCPM; (c) CHPCM

#### 3.2. Thermal properties of the CPCPM/diatomite composites

The DSC curves of the PCM, CPCPM and CHPCM are shown in Fig.2. Fig.2a shows the melting curves and the Fig.2b shows the solidifying curves. It can be seen that the melting and solidifying temperatures are 28.2 °C and 26.3 °C for PCM, 27.4 °C and 26.8 °C for the CPCPM, 27.0 °C and 26.9 °C for the CHPCM. The super-cooling degree is measured to be 1.9 °C for PCM, to be 0.6 °C for CPCPM and to be 0.1 °C for CHPCM. The super-cooling degree of CHPCM is lower than that of PCM, which means that the CHPCM can regulate the indoor temperature better.

The melting and solidifying latent heats of PCM are measured to be 146.2 and 144.1 kJ/kg, to be 85.3 and 77.8 kJ/kg for the CPCPM, and to be 17.1 and 16.2 kJ/kg for the CHPCM. The latent heat of the composites is proportional to the mass ratio because only PCM can take phase change process. So it can be calculated that the mass ratio of the CPCPM is 56.2% and that of CHPCM is 11.5%.

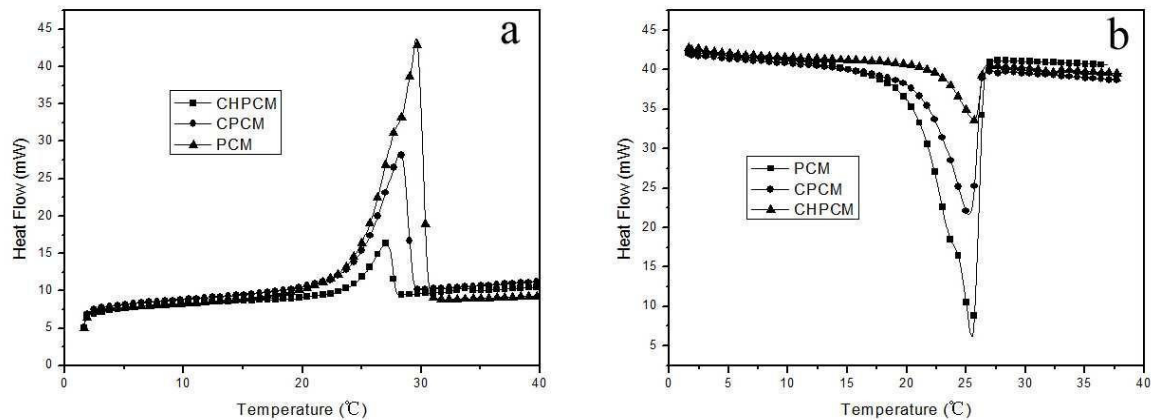


Fig. 2. The DSC curves of the PCM, CPCM and CHPCM (a) melting curves; (b) solidifying curves

### 3.3. Thermal stabilities of the CPCM/diatomite composites

Fig.3 presents the TGA curves of the PCM, CPCM and CHPCM. As can be seen from Fig.3, it is a two-step thermal degradation process for the composite. The first step occurs at the temperature between 130 °C and 250 °C, which is related to the thermal degradation of the PCM. The second step occurs at the temperature between 250 °C to 700 °C, which is related to the thermal degradation of the SiO<sub>2</sub> molecular. The temperature of maximum weight loss for PCM is 130 °C, and that of CPCM and CHPCM is 170°C. The results mean that the SiO<sub>2</sub> structure can improve the thermal stability of the composites.

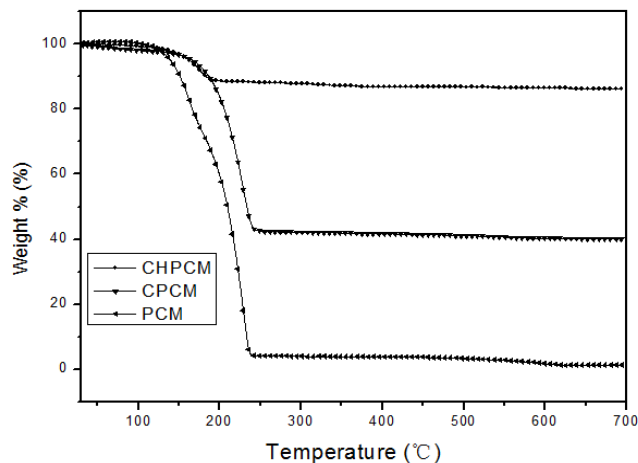


Fig. 3. The TGA curves of the PCM, CPCM and CHPCM

### 3.4. Hygroscopic properties of the CPCM/diatomite composites

The concept of moisture buffer value (MBV) was proposed by Rode et al [5]. The MBV indicates the amount of moisture uptake/release by the material when it is exposed to repeated daily variations in two given relatively humidity levels. The moisture uptake/release per open surface area and per % RH of the material from beginning to

end of the exposure to a new relative humidity is MBV.

The MBV is determined in an experiment where the sample is exposed to cyclic changes in RH between high and low for 8 hours and 16 hours respectively. There are two bottles containing different saturated salt solution. One bottle contains saturated KCl solution, which keeps the relative humidity inside at 88%. Another one contains saturated NaBr solution, which keeps the relative humidity inside at 62%. The sample hangs in the bottle with KCl solution, and then the bottle is sealed for 8 hours. Then the sample hangs in the bottle with NaBr solution, and the bottle is sealed for 16 hours. The process is alternative operated for at least 6 days. And the mass of the sample is measured with analytical balance every two hours.

Fig. 4 shows the practical mass change curves of CHPCM and diatomite. According to the experiment, it can be calculated that the MBV of the CHPCM is  $1.48 \text{ g/m}^2 \cdot \% \text{ RH}$ , and the MBV of the diatomite is  $0.33 \text{ g/m}^2 \cdot \% \text{ RH}$ . The limited class ranges from  $0.2 \text{ g/m}^2 \cdot \% \text{ RH}$  to  $0.5 \text{ g/m}^2 \cdot \% \text{ RH}$ . It can be seen that the MBV of CHPCM is within good class, and the MBV of diatomite is within limited class.

The moisture diffusion coefficient was measured by cup method. The saturated NaCl solution is kept in the bottle to keep the relative humidity of the air in container as 75%. The relative humidity outside is maintained at 52%. The results show that the moisture diffusion coefficient of the CHPCM is  $5.10 \times 10^{-10} \text{ kg/m}^2 \cdot \text{s}$ . The moisture diffusion coefficient of the diatomite is  $2.75 \times 10^{-10} \text{ kg/m}^2 \cdot \text{s}$ , which is lower than that of CHPCM.

The results indicate that the CPCM added in the diatomite can improve the hygroscopic properties of the diatomite. And the CHPCM has a good hygroscopic property, which means that it can be used to regulate the indoor relative humidity.

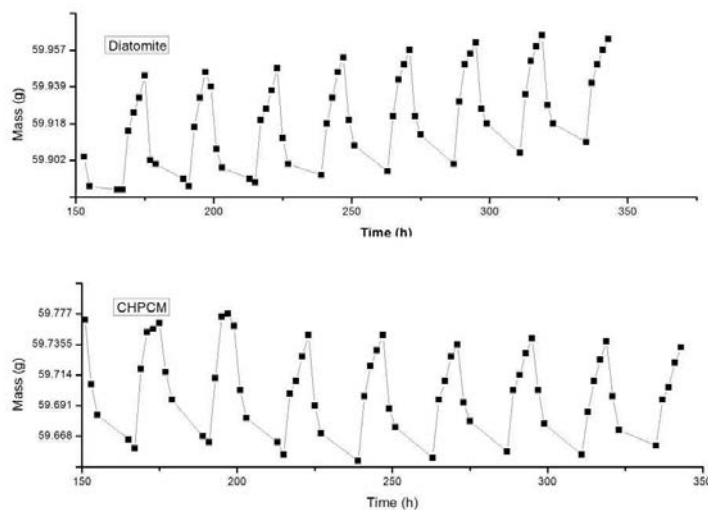


Fig. 4. The mass change curves of the diatomite and CHPCM

#### 4. Conclusions

This paper prepared a kind of hygroscopic phase change material with the phase change material and hygroscopic material. The  $\text{SiO}_2$  prepared with TEOS can prevent the melted PCM from leaking. And the measurement of thermal properties shows that the  $\text{SiO}_2$  can improve the thermal properties. The measurement of hygroscopic property shows that the CPCM can improve the hygroscopic property of the diatomite. The CPCM/diatomite composite can be used as indoor temperature and relative humidity control material.

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